
(12) UK Patent Application (19) GB (11) 2 027 686 A

(21) Application No 7927584

(22) Date of filing 8 Aug 1979

(23) Claims filed 8 Aug 1979

(30) Priority data

(31) 932964

(32) 11 Aug 1978

(33) United States of America
(US)

(43) Application published

27 Feb 1980

(51) INT CL³

C23F 11/16 E21B 41/02

(52) Domestic classification

C1C 253 302 463 A

E1F 45A 45E 45F 45G 45H

(56) Documents cited

GB 1382505

GB 1330516

GB 1142429

GB 1049044

GB 962954

GB 932877

GB 849126

GB 842091

GB 832015

(58) Field of search

C1C

E1F

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(54) Corrosion Inhibitor for Aqueous
Brines

(57) Corrosion of ferrous metals,
particularly metal goods in a wellbore,
by aqueous brines is inhibited by
including in the brine, an effective
amount of a dispersible sulfur

compound wherein the sulfur has an
oxidation state of zero or less.

Preferably, a quaternary pyridinium,
quinolinium or isoquinolinium salt is
also employed. Inclusion of a cobalt
salt is also sometimes desirable. The
sulfur compound is preferably
ammonium thiocyanate or thiourea.

Certain of the chemical formulae
appearing in the printed
specification were submitted in
formal form after the date of
filing.

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SPECIFICATION

Corrosion Inhibitor for Aqueous Brines

The invention relates to inhibiting corrosion of ferrous metals by aqueous brines. In a specific application for the petroleum industry, it relates to reducing corrosion of iron and steel casing, tubing, and other ferrous subterranean well structural parts exposed to aqueous brines used as completion, work over, or packer fluids.

In well treating operations, brines are utilized for various purposes, especially where a relatively dense aqueous fluid is desired. Alkali metal salt brines may be employed, but more typically, calcium chloride brines, calcium bromide brines, or a mixture thereof are employed because solutions of greater specific gravity may be obtained. Such brines are corrosive to the metal goods in the wellbore, even in the absence of substantially any oxygen. Such corrosion is relatively insignificant at temperatures of about 200°F, but becomes fairly significant at temperatures of at least 250°F, especially above about 300°F.

Although some corrosion inhibitor well suited for inhibiting HCl may find some utility in inhibiting brines, it cannot be said that a hydrochloric acid inhibitor will necessarily be effective in inhibiting brines, at least not to a practical degree.

Canadian Patent No. 983,041 teaches a water soluble corrosion inhibitor for brines comprising the reaction product of certain aliphatic saturated carboxylic acids with substituted imidazolines.

U.S. Patent No. 3,215,637 teaches that a mixture of sodium silicate and zinc chloride inhibits corrosion by sodium chloride and calcium chloride brines. The patent also discusses shortcomings of other known brine inhibitors such as sodium nitrate, hydrazine, pyrogallol, or sulphite.

U.S. Patent No. 4,010,111 discloses a corrosion inhibiting composition for aqueous brines wherein the inhibitor contains a reaction product of a carboxylic acid and a polyamine, an alcohol, and an alkylbenzene sulfonic acid.

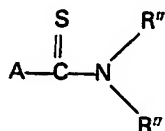
At the time of this invention, it is believed that among the most widely used commercial inhibitors for heavy brines—at least in the United States petroleum industry—were Baroid® Coat B-1400 inhibitor and Corexit® 7720 inhibitor. Analysis of a sample of the Baroid® product indicates it contains about 14 percent by weight of a volatile amine, about 19 percent by weight of isopropyl alcohol, about 45 percent by weight of water, and the balance predominantly ethoxylated amide with a small amount of carboxylic acid salt.

The present invention is based on the discovery that ferrous metals can be at least partially protected from corrosion by aqueous brines by including in the brine, an effective amount of a sulfur compound wherein the oxidation state of the sulfur is zero or less, which is uniformly dispersible in, and preferably soluble in, said brine and which is capable of making sulfur available for reaction with the ferrous metal to be protected to form a protective iron sulfide film on the surface of the metal exposed to the inhibited brine. Preferably, at least one quaternary pyridinium, quinolinium, or isoquinolinium salt which is soluble in the brine is also employed as an inhibitor aid.

Aqueous solutions of alkali metal halides may be inhibited using the composition of the present invention, although its greatest benefit is realized where the brine contains at least one polyvalent metal halide salt, such as calcium chloride, bromide, or iodide, zinc chloride, bromide, or iodide, or a mixture of such salts. Such brines are commonly used in oil field applications, as well as in other industries. For example, such brines may be used in separation processes wherein solids of different densities are separated by flotation. In addition to the corrosion inhibitor, such brines may contain various functional additives, if desired, such as fluid loss additives, gelling agents, friction reducers, or surfactants. Brine solutions which may be inhibited according to the present invention include aqueous organic acid solutions weighted with a suitable metal halide salt to increase the specific gravity thereof, although in most instances, solutions treated according to the present invention will normally have a slightly basic pH and will consist substantially of aqueous solutions of calcium or zinc halides or mixtures thereof.

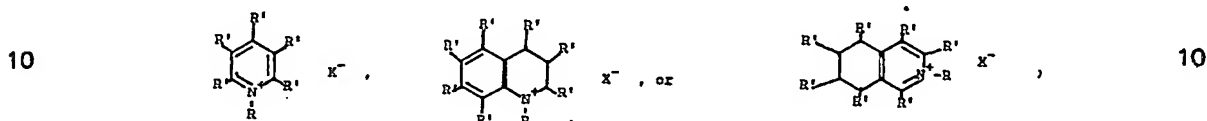
The corrosion inhibitor system of the present invention has good inhibitive properties, especially at the higher temperatures where the corrosion caused by brines would otherwise become relatively serious. It is also compatible with a wide range of functional additives. Moreover, particularly the most preferred embodiments act as a defoaming agent, thereby simplifying field mixing procedures.

The sulfur compound is preferably a water-soluble thio compound, e.g. a thiocyanate such as an alkali metal thiocyanate or, most preferably, ammonium thiocyanate. It can also be an organic thioamide and essentially any such compound is operable. This class of compounds includes thiourea-, a polythiourea, a hydrocarbon substituted derivative thereof, or a thioamide having the formula:



wherein A is a hydrocarbon radical of 1—12 carbon atoms or a pyridyl radical and each R' is a hydrogen atom or an alkyl radical of 1—8 carbon atoms. Thioamides such as thiourea, 1,2-diethylthiourea, propylthiourea, 1,1-diphenylthiourea, thiocarbanilide, 1,2-dibutylthiourea, dithiobiurea, thioacetamide, thionicotinamide, or thiobenzamide are representative of this class. Water soluble sulfides such as ammonium sulfide, an alkali metal sulfide, or corresponding hydrosulfide including H₂S are other operable thio compounds. Elemental sulfur which is dispersible in the brines is also operable, although the above mentioned soluble thio compounds are preferred.

Preferably, a quaternary pyridinium, quinolinium, or isoquinolinium salt which is stable in the aqueous brine solution is also employed as the inhibitor acid. Preferably, this salt has the formula:



where R is an alkyl radical of 1—20 carbon atoms, a benzyl radical, or an alkylated benzyl radical wherein the aromatic ring has one or more alkyl substituents totalling 1—20 carbon atoms, each R' is a hydrogen atom or an alkyl or alkoxy radical of 1—6 carbon atoms, and X is any convenient anionic radical such as halide, sulfate, acetate, or nitrate. Obviously, those skilled in the art will realize that the various parameters should not be selected to provide a compound having such a high carbon content that the compound is not soluble in the brine at at least an effective concentration. In the above general formulae, X is preferably a bromine or chlorine atom, and most preferably bromine. Preferably, R is a higher alkyl radical of about 6—16 carbon atoms. Also, R' is preferably hydrogen. Pyridinium salts are generally preferred. The most preferred embodiment considering both performance and solubility is n-octylpyridinium bromide. Mixtures of such salts may be employed if desired.

While any significant quantity of the sulfur compound will provide some degree of inhibition of corrosion, at least about 0.3 grams of the sulfur compound per liter of brine solution is usually required to provide practical protection. Concentrations as high as 20 grams of the inhibitor per liter are, for the most part, not detrimental. More than about 3 grams of the inhibitor per liter of brine, however, usually provides little or no additional protection, and in some cases may actually provide less protection than smaller amounts. The preferred upper limit of 3 grams per liter applies whether the sulfur compound is employed alone or in combination with the heterocyclic quaternary compound, i.e. when the quaternary compound is employed, the total concentration of the quaternary and sulfur compounds preferably does not exceed 3 g/liter. Most preferably, the total concentration of sulfur compound and quaternary salt is from about 0.5—2 grams per liter of brine.

If employed, the quaternary salt is employed in an amount which is effective to improve the overall inhibition of the system. The optimum ratio of the quaternary salt to the sulfur compound will vary somewhat from system to system, but generally, benefit is realized when the two components are employed in a weight ratio of from 0.1:1 to 10:1, although a ratio of from 0.125:1 to 4:1 is more preferred. A ratio of 0.2:1 to 1:1 is most preferred, especially where the concentration of the components approaches the upper or lower limits recommended in the preceding paragraph. For any given brine system and combination of inhibitor components, those skilled in the art will be able to arrive at an optimum concentration and ratio.

The addition of a small but effective amount—e.g., from 0.05 to 0.5 gram Co⁺² per liter of brine—of a water soluble cobalt salt to the system also improves its effectiveness, but is not necessary for an operable or even commercially acceptable performance. Consequently, though somewhat better performance is obtained with the cobalt, it is not normally a preferred embodiment for routine applications because of somewhat increased toxicity and environmental concerns. If employed, the cobalt may be provided by essentially any cobaltous compound which is sufficiently soluble in the aqueous brine solution to provide the desired concentration of cobaltous ions. Salts such as CoCl₂, CoBr₂, CoSO₄, Co(NO₃)₂, cobaltous acetate, or cobaltous benzoate are all suitable sources of cobaltous ions. Salts such as the acetate, benzoate, or bromide are particularly preferred.

The present invention is further illustrated by the following examples and comparison runs.

Test Procedure:

In preparation for the corrosion tests hereinafter described, coupons were cut from 2-3/8" O.D. N80 steel tubing. The coupons were cleaned by tumbling in aluminum oxide grit after which they were exposed to an ultrasonic trichloroethylene bath, rinsed in acetone, dried, and stored in a desiccator. In carrying out the tests, the coupon was placed in the test solution in an autoclave and the test temperature and pressure were established as rapidly as was practical. Stated test times are the times for which the coupon was exposed to the solution of the specified temperature and pressure. All tests were carried out under static conditions, i.e. without agitation, at 1000 psi. After permitting the test bath to cool to about 150°F, the coupon was removed from the bath, rinsed in acetone, and washed in inhibited 15% aqueous HCl for about 3—4 minutes with agitation to dissolve the iron sulfide film

which forms during the test. The coupon was then washed in water, scrubbed with a brass brush and pumice soap, heated in hot water to accelerate acetone evaporation, rinsed in acetone, dried, cooled, and weighed.

In all corrosion tests, the various additives in the quantities stated were added to 100 ml of the brine. In all tables, "Corrosion Rate" is expressed as pounds per square foot per the stated test time. "Percent Inhibition" is the following quantity:

$$\frac{\text{Corrosion rate with no inhibitor—Corrosion rate of test solution}}{\text{Corrosion rate with no inhibitor}} \times 100.$$

Various quaternary salt solutions were prepared and used as follows:

- 10 Prep. A: Decylquinolinium bromide (DQBr)
 Prep. B: Dodecylquinolinium bromide (DodQBr)
 Prep. C: Tetradecylpyridinium bromide (TdPBr)
 Prep. D: Hexadecylpyridinium bromide (HdPBr)
 Prep. E: Decylpyridinium bromide (DPBr)
 15 Prep. F: Dodecylpyridinium bromide (DodPBr)
 Prep. G: Alkyl substituted tetradecylpyridinium bromide (AlkTdPB)
 Prep. H: Hexylpyridinium bromide (HPBr)
 Prep. I: Octylpyridinium bromide (OPBr)
 Prep. J: 0.4:1 OPBr:Ammonium thiocyanate
 Prep. K: 0.26:1 OPBr:Ammonium thiocyanate

20 Several series of corrosion tests summarized in the following tables were carried out. 20

Series One

Aqueous Brine: 52 weight percent CaBr_2

Temperature: 350°F

Time: 68 hours

25	Inhibitor			Oxygen Scavenger	Corrosion Rate	25
	Run	Quaternary Compound	Thio Compound			
	1		—	—	.0163; .013	
	2	0.5 ml Prep E (DPBr)	—	—	0.0187	
	3	0.5 ml Prep E (DPBr)	0.3 g thiourea	—	0.0040	
30	4	0.5 ml Prep E (DodPBr)	—	—	0.0181	30
	5	0.5 ml Prep F (DodPBr)	0.3 g thiourea	—	0.0052	
	6	0.5 g Prep C (TdPBr)	—	—	0.0152	
	7	0.5 g Prep C (TdPBr)	0.3 g thiourea	—	0.0062	
	8	0.5 g Prep D (HdPBr)	—	—	0.0167	
35	9	0.5 g Prep D (HdPBr)	0.3 g thiourea	—	0.0099	35
	10	0.5 ml Prep A (DQBr)	0.3 g thiourea	—	0.0098	
	11	0.5 ml Prep B (DodQBr)	0.3 g thiourea	—	0.0082	
	12	Note 1	0.3 g thiourea	Note 1	0.0067	
	13	Note 2	0.3 g thiourea	Note 2	0.0101	
40	14	0.5 ml Prep G (AlkTdPB)	0.3 g thiourea	—	0.0053	40
	15	—	0.3 g NH_4SCN	0.5 ml	0.0056	
	16	—	0.3 g NH_4SCN	Coraxit 7720 1.0 ml	0.0045	
45	17	0.25 ml Prep E (DPBr)	0.3 g NH_4SCN	—	0.0039	45
	18	0.5 ml Prep E (DPBr)	0.3 g NH_4SCN	—	0.0039	
	19	0.25 ml Prep H (HPBr)	0.3 g NH_4SCN	—	0.0061	
	20	0.5 ml Prep H (HPBr)	0.3 g NH_4SCN	—	0.0062	
	21	0.25 ml Prep I (OPBr)	0.3 g NH_4SCN	—	0.0049	
50	22	0.5 ml Prep I (OPBr)	0.3 g NH_4SCN	—	0.0045	50
	23	0.5 ml Prep G (AlkTdPB)	0.3 g NH_4SCN	—	0.0048	
	24	0.5 ml Prep E (DPBr)	0.3 g NH_4SCN	—	0.0098	
	25	—	0.3 g NH_4SCN	0.3 g $\text{Na}_2\text{S}_2\text{O}_4$	0.0069	
55	26	—	—	0.3 g $\text{Na}_2\text{S}_2\text{O}_4$	0.0091	55
	27	—	—	0.6 g $\text{Na}_2\text{S}_2\text{O}_4$	0.0161	

Notes:

- (1) 0.5 ml of 1 part isopropanol, 4 parts the reaction product of 1-dodecyl bromide and triethyl amine.
 (2) 0.5 ml of 1 part isopropanol, 4 parts the reaction product of 1-dodecyl bromide and triethanol amine.
 5 (3) The corrosion rates for Runs 2—14 are best compared with the 0.0163 rate for Run 1, and the rates for Runs 15—27 with the 0.0137 rate for the rerun of Run 1 since those groups of runs were made on the same days, respectively. 5

Series TwoAqueous Brine: 52 weight percent CaBr_2

10 Temperature: 350°F

10.

Time: 16 hours

Run	Inhibitor			Oxygen Scavenger	Corrosion Rate	
	Quaternary Compound	Thio Compound	Other			
15	28 0.1 ml diluted Prep E ⁽¹⁾	0.3 g thiourea	—	—	0.0040	15
	29 0.25 ml diluted Prep E ⁽¹⁾	0.3 g thiourea	—	—	0.0037	
	30 0.5 ml diluted Prep E ⁽¹⁾	0.3 g thiourea	—	—	0.0025	
	31 1.0 ml diluted Prep E ⁽¹⁾	0.3 g thiourea	—	—	0.0025	
	32 0.25 ml Prep E (DPBr)	0.3 g thiourea	—	—	0.0026	20
	33 0.25 ml Prep E (DPBr)	0.05 g thiourea	—	—	0.0034	
20	34 0.25 ml Prep E (DPBr)	0.1 g thiourea	—	—	0.0025	
	35 0.25 ml Prep E (DPBr)	0.2 g thiourea	—	—	0.0028	
	36 0.5 ml Prep H (HPBr)	0.3 g thiourea	—	—	0.0033	
	37 0.5 ml Prep I (OPBr)	0.3 g thiourea	—	—	0.0028	
	38 0.5 ml Prep F (DodPBr)	0.3 g thiourea	—	—	0.0026	25
25	39 0.5 ml Prep C (TdPBr)	0.3 g thiourea	—	—	0.0028	
	40 See Note 1, Series one	0.3 g thiourea	See Note 1, Series One	—	0.0033	
	41 —	—	—	—	0.0054	

Note:

- 30 (1) 1 ml Prep E (DPBr) diluted with 9 ml water.

30

Series ThreeAqueous Brine: 852 g CaCl_2 dissolved in 2500 ml of 52% CaBr_2

Temperature: 350°F

Time: 16 hours

Run	Inhibitor			Oxygen Scavenger	Corrosion Rate	
	Quaternary Compound	Thio Compound	Other			
35	42 —	—	—	—	0.0079	35
	43 —	—	2 ml Baroid 1400	—	0.0072	
40	44 —	—	1 ml Corexit 7720	—	0.0068	40
	45 0.5 ml Prep E (DPBr)	0.3 g NH_4SCN	—	—	0.0030	45
	46 0.5 ml Prep E (DPBr)	0.6 g NH_4SCN	—	—	0.0031	
	47 Note 1	0.3 g NH_4SCN	Note 1	—	0.0040	
45	48 Note 1	0.6 g NH_4SCN	Note 1,	—	0.0043	
	49 See Note 2, Series One	0.3 g NH_4SCN	See Note 2, Series One	—	0.0026	
	50 See Note 2, Series One	0.6 g NH_4SCN	See Note 2, Series One	—	0.0026	
50	51 0.5 ml Prep F (HdPBr)	0.3 g NH_4SCN	—	—	0.0028	50
	52 0.5 ml Prep F (HdPBr)	0.6 g NH_4SCN	—	—	0.0029	
	53 —	0.6 g NH_4SCN	—	—	0.0038	

Note:

- (1) 0.5 g of 1 part isopropanol, 4 parts the reaction product of 1-dodecyl bromide and triethyl amine.

Series Four

Aqueous Brine: 852 g CaCl₂ dissolved in 250 ml of 52% CaBr₂

Temperature: 350°F

Time: 118 hours

Run	Inhibitor	Corrosion Rate	Percent Inhibition	
54	—	0.0202	Control	5
55	0.1 ml Prep J (0.4:1 OPBr:NH ₄ SCN)	0.0178	13	
56	0.2 ml Prep J (0.4:1 OPBr:NH ₄ SCN)	0.0150	26	
10 57	0.4 ml Prep J (0.4:1 OPBr:NH ₄ SCN)	0.0101	50	10
58	0.6 ml Prep J (0.4:1 OPBr:NH ₄ SCN)	0.0086	57	
59	0.1 ml Prep K (0.26:1 OPBr:NH ₄ SCN)	0.0180	11	
60	0.2 ml Prep K (0.26:1 OPBr:NH ₄ SCN)	0.0128	37	
61	0.4 ml Prep K (0.26:1 OPBr:NH ₄ SCN)	0.0095	53	
15 62	0.6 ml Prep K (0.26:1 OPBr:NH ₄ SCN)	0.0078	61	15
63	0.2 ml Baroid 1400	0.0167	17	
64	0.4 ml Baroid 1400	0.0155	23	
65	0.6 ml Baroid 1400	0.0186	8	
66	0.2 ml Corexit 7720	0.0168	17	
20 67	0.4 ml Corexit 7720	0.0180	11	20

Series Five

Aqueous Brine: 852 g CaCl₂ dissolved in 250 ml of 52% CaBr₂

Temperature: 300°F

Time: 72 hours

Run	Inhibitor	Corrosion Rate	Percent Inhibition	
68	—	0.0101	Control	25
69	0.1 ml Prep K (0.26:1 OPBr:NH ₄ SCN)	0.0072	29	
70	0.2 ml Prep K (0.26:1 OPBr:NH ₄ SCN)	0.0049	51	
30 71	0.4 ml Prep K (0.26:1 OPBr:NH ₄ SCN)	0.0027	73	30
72	0.6 ml Prep K (0.26:1 OPBr:NH ₄ SCN)	0.0026	73	
73	0.1 ml Baroid 1400	0.0100	1	
74	0.2 ml Baroid 1400	0.0085	16	
75	0.4 ml Baroid 1400	0.0081	20	
35 76	0.1 ml Corexit 7720	0.0091	10	35
77	0.2 ml Corexit 7720	0.0067	34	
78	0.4 ml Corexit 7720	0.0050	50	
79	0.1 ml Dowell A163 ⁽¹⁾	0.0106	-5	
80	0.2 ml Dowell A163 ⁽¹⁾	0.0098	5	
40 81	0.4 ml Dowell A163 ⁽¹⁾	0.0078	23	40

Note:

(1) Dowell A 163 is an inhibitor of the imidazoline type.

Series Six

Temperature: 350°F

Time: 72 hours

Run	Brine	Inhibitor	Corrosion Rate	Percent Inhibition	
82	19% ZnBr ₂ , 46% CaBr ₂	—	0.0245	Control	
83	19% ZnBr ₂ , 46% CaBr ₂	0.4 ml Prep K (0.26:1 OPBr:NH ₄ SCN)	0.0035	86	
50 84	29% ZnBr ₂ , 41% CaBr ₂	—	0.0207	Control	50
85	29% ZnBr ₂ , 41% CaBr ₂	0.4 ml Prep K (0.26:1 OPBr:NH ₄ SCN)	0.0043	79	
86	57% ZnBr ₂ , 20% CaBr ₂	—	0.1494	Control	
87	57% ZnBr ₂ , 20% CaBr ₂	0.4 ml Prep K (0.26:1 OPBr: NH ₄ SCN)	0.0521	65	

Claims

- 55 1 A method of reducing the corrosive effect of aqueous brine on ferrous metal surfaces which are contacted by the brine, comprising adding to the brine a corrosion inhibiting quantity of a sulfur compound wherein the oxidation state of the sulfur is zero or less, said sulfur compound being uniformly dispersible in the brine. 55

2. A method as claimed in claim 1, wherein the sulfur compound is employed in an amount of at least 0.3 grams per liter of brine.

3. A method as claimed in claim 1 or claim 2, wherein the sulfur compound is a water soluble thiocyanate or thioamide.

4. A method as claimed in claim 3, wherein the sulfur compound is ammonium thiocyanate or thiourea.

5. A method as claimed in any one of the preceding claims, wherein the brine contains at least one of calcium chloride, calcium bromide, calcium iodide, zinc chloride, zinc bromide, and zinc iodide.

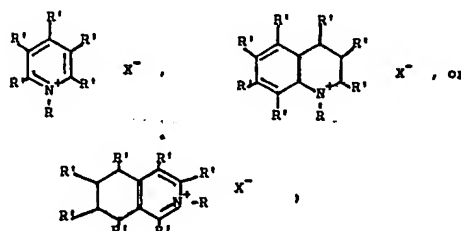
6. A method as claimed in any one of the preceding claims wherein an effective amount of at least one quaternary pyridinium, quinolinium, and isoquinolinium salt is added to the brine to further reduce the corrosive effect of the brine, said quaternary salt being selected so as to be sufficiently soluble in the brine so that an effective amount can be dissolved in the brine.

7. A method as claimed in claim 6, wherein the combined weight of said sulfur compound plus any quaternary salt present does not exceed 3 grams per liter.

8. A method as claimed in claim 6 or claim 7, wherein the quaternary salt is employed in an amount of from 0.1 to 10 parts per part by weight of the sulfur compound.

9. A method as claimed in claim 7 or claim 8, wherein the total concentration of the sulfur compound and the quaternary salt is from 0.5 to 2 grams per liter of brine, and the weight ratio of said quaternary compound to sulfur is from 0.125:1 to 4:1.

10. A method as claimed in any one of claims 6 to 9, wherein the quaternary salt has the formula



where R is an alkyl radical of 1—20 carbon atoms, a benzyl radical, or an alkylated benzyl radical wherein the aromatic ring has one or more alkyl substituents totalling 1—20 carbon atoms, each R' is independently a hydrogen atom or an alkyl or alkoxy radical of 1—6 carbon atoms, and X is an anionic radical.

11. A method as claimed in claim 10, wherein R is an alkyl radical of 6—16 carbon atoms.

12. A method as claimed in claim 10 or claim 11, wherein X is bromine.

13. A method as claimed in any one of claims 10 to 12, wherein each R' is hydrogen.

14. A method as claimed in claim 10, wherein the quaternary compound is a N-octyl pyridinium bromide.

15. A method as claimed in any one of the preceding claims, wherein an effective amount of a water soluble cobalt salt is added to the brine to still further reduce the corrosive effect of the brine.

16. A method as claimed in claim 1 substantially as hereinbefore described with reference to any one of Runs 3, 5, 7, 9 to 25, to 40, 45 to 53, 55 to 62, 69 to 72, 83, 85 and 87.

17. Brine to which has been added a corrosion inhibiting quantity of a sulfur compound wherein the oxidation state of the sulfur is zero or less, said sulfur compound being uniformly dispersible in the brine.

18. A well treating operation involving the use of brine as claimed in claim 17.

19. A separation process, wherein solids of different densities are separated by flotation, involving the use of brine as claimed in claim 17.

20. Petroleum, or a petroleum derivative, which has been recovered as a result of a well treating operation as claimed in claim 18.

21. Ferrous metal having a protective iron sulfide film thereon, which film has been provided by contacting a ferrous metal surface with brine as claimed in claim 17.

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